How to model surface diffusion using the phase-field approach

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(Dated: February 6, 2008)

It is demonstrated that the description of surface-diffusion controlled dynamics via the phase-field method is less trivial than it appears at first sight. A seemingly straightforward approach previously used in the literature is shown to fail to produce the correct asymptotics, albeit in a subtle manner. An apparently obvious alternative fails for a complementary reason. Finally, a model is constructed that asymptotically approaches known sharp-interface equations without adding undesired constraints. In order to provide a complete physical example, the model is exhibited for the elastically induced Grinfeld instability with material transport by surface diffusion. The whole analysis is carried out for three-dimensional systems to pave the way for simulations in $\mathbb{R}^3$.

PACS numbers: 68.35.Fx Surface diffusion; 02.70.-c Computational techniques; 47.20.Hw Morphological instability, phase changes; 46.25.-y Static elasticity
Keywords: Surface diffusion, phase-field model, tensorial mobility

I. INTRODUCTION

For a large class of pattern-forming systems, the essential dynamics to be understood and described is that of an interface between two phases. Mathematically speaking, the problem to be solved consists in determining the position of the interface as a function of time, i.e., it is a free or moving-boundary problem.

Phase-field models have been established as powerful tools for the numerical simulation of this kind of problem. They avoid explicit front tracking and are versatile enough to deal with topological changes. In a phase-field model, information on the interface position is present implicitly, given either as a level set of a particular value of the phase field (in two-phase models) or by equality of the phase-field values for different phases (in multi-phase models), and can be recovered by computation of the appropriate level set at only those times when knowledge of the position is desired.

A major field of application are solidification problems, where diffuse-interface models were developed early on [1, 2, 3] and have seen renewed interest ever since computational power increased enough to render their simulation feasible. The concept was extended to anisotropic interface properties [4], and first qualitative numerical calculations of dendritic growth [5, 6] were followed by theoretical improvement of the asymptotics permitting quantitative simulations [7, 8], at least for intermediate to large undercoolings. Non-dendritic growth morphologies were also simulated, even in three dimensions [9]. Generalizations included the description of the coexistence of more than two phases [10, 11].

Additional examples of successful application of the tool phase field include the modeling of step flow growth [12, 13] and of the elastically induced morphological instability [14, 15, 16], often labeled Grinfeld [17] or Asaro-Tiller-Grinfeld (ATG) instability [18]. All of the examples mentioned so far dealt with *nonconservative* interface dynamics, where a particle reservoir is provided by either the melt that is in contact with the solid or the adatom phase on a vicinal surface.

Actually, regarding the ATG instability, which is an instability with respect to material transport driven by elastic energy, interest initially focused on transport by surface diffusion, which leads to *conserved* dynamics. This is the case in the first article by Asaro and Tiller [18], but also in the first numerical simulations by sharp-interface continuum models [19], preceding computations of the instability under transport by melting-crystallization [20].

The situation reversed, when the phase-field method was for the first time employed to compute the ATG instability [14, 15]. Here all the early works considered a nonconserved phase-field [14, 15, 16, 21]. In fact, there seem to be no publications so far treating conserved phase-field dynamics in this system. This difference in preferences when modeling either on the basis of a sharp-interface model or using a phase field may be due to the fact that writing down a nonconservative and a conservative model is equally simple in the former case, whereas it is less straightforward to write down the conservative model within the phase-field approach – correctly – than the nonconservative one. The demonstration of this assertion will be a major point to be made in the present article.

This is not to say that phase-field models with a conservation law for the phase field have not been considered at all. Starting from a Cahn-Hilliard equation with a concentration dependent mobility, Cahn et al. [22] obtained an interface equation with the normal velocity proportional to the Laplacian of the mean curvature. It then looks as if all phase-field models with surface diffusion should be derivable on the basis of similar considerations. Indeed, comparable models have been applied in the simulation of electromigration and voiding in thin metal films [23, 24]. These two models are slightly different, but the difference is not crucial and all previous models seem to suffer from the same problem, to be discussed in the following.

As we shall see, it is quite easy to set up a conservative phase-field model. But it is more difficult to obtain the correct asymptotics describing surface diffusion as given by the desired sharp-interface limit. Past models such as the ones presented in [22, 23, 24] describe this asymptotics *almost* correctly, but not quite. The purpose of this article is to point out

the reasons, to explore an alternative approach and finally, to give a model that is asymptotically correct.

To be definite, I shall consider the case of surface diffusion in the ATG instability. The paper is organized as follows. In Sec. II, the sharp-interface model to be approximated by the phase-field equations is specified. Section III then presents the standard approach that previously was supposed to reduce to the correct limit and pinpoints the oversight in hitherto existing asymptotic analyses. An alternative approach is presented in Sec. IV failing for complementary reasons. By an appropriate combination of the ideas from both approaches, I will then arrive at a phase-field model in Sec. V that may lack elegance but has the virtue of giving the correct asymptotic behaviour and doing so at a lower effective expansion order than the preceding models. All derivations are given for the three-dimensional case. While this is slightly more involved than with the two-dimensional model, it is expected that future interesting applications will be three-dimensional. Phase-field models for conserved dynamics considered so far have been restricted to two dimensions. Moreover, the tensorial nature of the elasticity part of the model makes a generalization from two to three dimensions less straightforward than with scalar or vector equations. Section VI contains some concluding remarks. A number of mathematical details from differential geometry as well as the asymptotics of the elastic part of the model, which is unproblematic, are relegated to various appendices.

II. SHARP-INTERFACE MODEL FOR THE ATG INSTABILITY UNDER SURFACE DIFFUSION

One of the more convenient descriptions of the ATG instability starts from an expression for the local chemical potential difference between the solid and the second phase [liquid, gas (vapour), or vacuum] at the interface. In three dimensions, this is given by [25]

$$\begin{aligned}\delta\mu \;=\; & \frac{1}{2E\rho_s}\Big\{(1+\nu)\sum_{i,j}\left(\sigma_{ij}-\sigma_{nn}\delta_{ij}\right)^2 \\ & -\nu\Big[\sum_k(\sigma_{kk}-\sigma_{nn})\Big]^2\Big\} \\ & +\frac{1}{\rho_s}\gamma(\kappa_1+\kappa_2)\;. \end{aligned} \tag{1}$$

In this equation, the material parameters are Young's modulus E, the Poisson number ν, meaning that we assume isotropic elastic properties, the surface tension γ, assumed isotropic as well for simplicity, and the density ρ_s of the solid phase. The σ_{ij} are the (cartesian) components of the stress tensor, σ_{nn} is its normal component at the interface, κ_1 and κ_2 are the two principal curvatures of the interface at the point considered. Their sum is commonly denoted as mean curvature.

In writing equation (1), we have neglected a gravitational contribution to the chemical potential [16] that usually is unimportant in situations, where surface diffusion governs the dynamics. For example, in the self-organized formation of patterns under strain built up during molecular beam epitaxy of semiconductor heterostructures, the strain energy induced by lattice mismatch exceeds any potential energy in the gravitational field by several orders of magnitude.

To determine the stresses needed in the calculation of the chemical potential, one has to solve the elastic equations. These are given by the mechanical equilibrium condition of vanishing divergence of the stress tensor,

$$\sum_j \frac{\partial\sigma_{ij}}{\partial x_j}=0\,, \tag{2}$$

where volume forces such as gravity are assumed to be absent and we have restricted ourselves to the static limit of elasticity (hence there are no sound waves), plus a constitutive equation, for which linear elasticity, described by Hooke's law

$$\sigma_{ij}=\frac{E}{1+\nu}\Big(u_{ij}+\frac{\nu}{1-2\nu}\sum_k u_{kk}\,\delta_{ij}\Big)-p_0\delta_{ij}\,, \tag{3}$$

is assumed, in which

$$u_{ij}=\frac{1}{2}\left(\frac{\partial u_i}{\partial x_j}+\frac{\partial u_j}{\partial x_i}\right) \tag{4}$$

is the (small-)strain tensor. It is convenient to choose the hydrostatic strain state assumed by the solid under the equilibrium pressure p_0 of the non-solid phase as reference state, hence the term $-p_0\delta_{ij}$ (p_0 may of course be zero). This simply means that we are measuring displacements of material points starting from their position in this state. The issue of reference states and their appropriate choice is discussed at length in [16].

The elastic equations must be supplemented with boundary conditions, of which only the boundary conditions at the interface between the two phases need to be specified here:

$$\sigma_{nn}=-p,\quad \sigma_{nt_1}=\sigma_{nt_2}=0\,, \tag{5}$$

that is, the normal component of the stress is equal to the negative external pressure, while its shear components along two independent tangents $\mathbf{t}_1$ and $\mathbf{t}_2$ vanish. By assuming a continuous component σ_{nn}, the pressure jump at a curved interface due to capillary overpressure is neglected, an approximation that is well-justified under a wide range of conditions. For a discussion of the validity of this approximation as well as the others mentioned, see [26].

Once the chemical potential has been computed, the stability of the interface can be assessed, but in order to determine its evolution, some dynamical law governing its motion must be stated. If a particle reservoir is present and the interface is rough, it is natural to assume linear nonequilibrium kinetics. The driving force then is the chemical potential difference itself, and the normal velocity v_n of the interface will be proportional to it: $v_n=-k_v\delta\mu$, where k_v is a mobility and the normal points from the solid into the second phase. For material transport by surface diffusion, the driving force is the gradient of the chemical potential along the surface instead, producing a surface current $j\propto-\nabla_s\,\delta\mu$ (∇_s is the surface gradient), which leads to a dynamical law of the form

$$v_n=D_s\,\Delta_s\delta\mu\,, \tag{6}$$

where Δ_s is the Laplace-Beltrami operator on the surface and D_s a diffusion coefficient, assumed constant here.

Equations (1) through (6) constitute the continuum model for the ATG instability with transport by surface diffusion, to which a phase-field model should converge in the limit of asymptotically small interface width.

III. SCALAR-MOBILITY PHASE-FIELD MODEL

Before discussing the structure of previous phase-field models attempting to capture surface diffusion dynamics, let us briefly recall the phase-field model for nonconserved order parameter ϕ. This can be written [16]

$$\frac{\partial\phi}{\partial t} = \frac{k_v\gamma}{\rho_s}\Big\{\nabla^2\phi - \frac{1}{\epsilon^2}\big[2f'(\phi) + \frac{\epsilon}{3\gamma}h'(\phi)V_{\rm el}\big]\Big\} \qquad (7)$$

where $f(\phi) = \phi^2(1-\phi)^2$ is the usual double-well potential describing two-phase equilibrium and $h(\phi) = \phi^2(3-2\phi)$ may be interpreted as the local solid fraction, varying between 1 in the solid phase (i.e., for $\phi = 1$) and 0 in the non-solid phase ($\phi = 0$). Primes denote derivatives with respect to the argument. $h(\phi)$ has the convenient property that it has extrema at $\phi = 0$ and $\phi = 1$, the location of the minima of the double-well potential. $V_{\rm el}$ is given by

$$V_{\rm el} = G\sum_{i,j} u_{ij}^2 + \frac{\lambda-\tilde\lambda}{2}\Big(\sum_k u_{kk}\Big)^2 , \qquad (8)$$

where $G = E/[2(1+\nu)]$ is the shear modulus or first Lamé constant, $\lambda = E\nu/[(1+\nu)(1-2\nu)]$ the second Lamé constant, and $\tilde\lambda$ is the bulk modulus of the non-solid phase (if this is vacuum, $\tilde\lambda = 0$).

In the diffuse-interface formulation, the elastic equations take the following form

$$\begin{aligned}\sum_j \frac{\partial\tilde\sigma_{ij}}{\partial x_j} &= 0\,,\\ \tilde\sigma_{ij} &= h(\phi)\,\sigma_{ij} - [1-h(\phi)]\,p\,\delta_{ij}\,,\end{aligned} \qquad (9)$$

where σ_{ij} is given by (3) and $p = p_0 - \tilde\lambda\sum_k u_{kk}$.

The standard approach to a phase-field description of surface diffusion, as proposed in [22, 23, 24], is then to prepend the right hand side of Eq. (7) with a differential operator corresponding to the divergence of a gradient multiplied by a phase-field dependent mobility, i.e., Eq. (7) becomes replaced with

$$\begin{aligned}\frac{\partial\phi}{\partial t} &= \nabla\cdot M\nabla\frac{1}{\epsilon^2}\,\delta\mu(\nabla^2\phi,\phi)\,,\\ \delta\mu(\nabla^2\phi,\phi) &\equiv -\epsilon^2\nabla^2\phi + 2f'(\phi) + \frac{\epsilon}{3\gamma}h'(\phi)V_{\rm el}\,,\end{aligned} \qquad (10)$$

where M is a scalar function of either ϕ [22, 24] or $\epsilon\nabla\phi$ [23], chosen such that the mobility tends to zero far from the interface: $M(\phi,\epsilon\nabla\phi)\to 0$ for $\phi\to 0$ and $\phi\to 1$. The elastic equations remain unchanged, i.e., while the nonconservative model is given by Eqs. (7) through (9), the conservative model is given by Eqs. (8) through (10).

At this point, a few remarks are in order. First, the field ϕ is the density of a conserved quantity by construction, since the right hand side of (10) is written as a divergence. This is true for any (nonsingular) form of the mobility. Second, $\delta\mu$ becomes zero for $\phi\to 0$ and $\phi\to 1$, meaning that there is no diffusion in the bulk anyway. One might therefore wonder whether it is really necessary to choose a mobility that goes to zero in the bulk. The conservation law plus the absence of diffusion far from the interface should suffice to restrict transport to diffusion along the interface. In fact, we shall see that essentially the same asymptotic results are obtained no matter what the form of M, the only conditions to be imposed being positivity (for almost all values of ϕ or $\nabla\phi$) and boundedness. It is just easier to derive them if it is in addition assumed that M vanishes in the bulk. On the other hand, it will turn out that if a restriction imposed by the asymptotics is removed (or not yet satisfied in the temporal evolution of the system), M has to decay sufficiently fast inside the bulk for the limit to make sense. This may be relevant for the behaviour of the model before it reaches its asymptotic state.

Finally, the issue at present is not so much whether the dynamics is conservative but whether it does reduce to the sharp-interface model of Sec. II in the limit of an asymptotically vanishing interface thickness. To investigate this, we have to explicitly carry out the asymptotic analysis.

A. Local coordinate system

The basic idea of the analysis is to expand all dynamical quantitities in terms of the small parameter ϵ describing the interface thickness, to solve for the phase field and to use the solution to eliminate its explicit appearance from the equations. To this end, the domain of definition of the field is divided into an outer region, where gradients of the fields can be considered to be of order one and an inner region (close to the interface), where these gradients are of order $1/\epsilon$. The expansion in powers of ϵ is rather straightforward in the outer domain, Eqs. (8) through (10) can be taken directly as a starting point. As to the inner domain (and its matching with the outer region), it is useful to first transform to coordinates adapted to its geometry. Therefore, a coordinate r is introduced that is orthogonal to the interface (defined as the level set corresponding to $\phi(x,y,z,t) = 1/2$) and two coordinates s and q that are tangential to it. r is the signed distance from the interface and will be rescaled by a stretching transformation $r = \epsilon\rho$ to make explicit the ϵ dependence for the expansion. Inner and outer solutions must satisfy certain matching conditions due to the requirement that they agree in the combined limit $\epsilon\to 0$, $\rho\to\pm\infty$, $r\to 0$. These conditions are given in App. A.

To obtain a basis for our local coordinate system, we first write

$$\mathbf{r} = \mathbf{R}(s,q) + r\,\mathbf{n}(s,q) \qquad (11)$$

where $\mathbf{r}$ is the position vector of a point near the interface,

R the position of the interface itself, and **n** the normal vector on it (oriented the same way as in the sharp-interface model, i.e., pointing out of the solid). Next, we require the coordinates s and q parametrizing the interface to be both orthogonal and arclength-like, meaning that the tangential vectors $\mathbf{t}_1 \equiv \partial\mathbf{R}/\partial s$, $\mathbf{t}_2 \equiv \partial\mathbf{R}/\partial q$ are orthogonal and that they are unit vectors. It is shown in the App. B that the requirement of both coordinates being arclengths is less innocent than it seems – it implies that the coordinate lines are geodesics, which is a strong restriction. (On a planar surface, only cartesian coordinate systems satisfy this condition.) It may be worthwhile to point out a difference between the two- and three-dimensional cases here. In two dimensions, the local coordinate system can essentially always be chosen global in the tangential coordinate, for which we may take the arclength. Locality is only necessary in r (this coordinate may turn singular for a curved interface, when the distance from the latter reaches the radius of curvature). In three dimensions, an interface with a nontrivial topology does not permit a description by a single coordinate patch, so in general the coordinates s and q have to be local, too. However, for the asymptotic analysis, we never need to compare far-away points along the interface, so a coordinate patch that is valid in the neighbourhood of a point $\mathbf{R}(s_0, q_0)$ is quite sufficient, and we can choose, without loss of generality, a geodesic coordinate system, despite the fact that this will not necessarily be global even on a curved interface with the topology of the plane.

Given the coordinates, it is a trivial matter to write down a coordinate basis

$$\begin{aligned}
\mathcal{E}_r &\equiv \frac{\partial \mathbf{r}}{\partial r} = \mathbf{n}(s,q)\,, \\
\mathcal{E}_s &\equiv \frac{\partial \mathbf{r}}{\partial s} = \frac{\partial \mathbf{R}}{\partial s} + r\frac{\partial \mathbf{n}}{\partial s} = (1+r\kappa_1)\,\mathbf{t}_1 + r\tau_1\mathbf{t}_2\,, \\
\mathcal{E}_q &\equiv \frac{\partial \mathbf{r}}{\partial q} = \frac{\partial \mathbf{R}}{\partial q} + r\frac{\partial \mathbf{n}}{\partial q} = (1+r\kappa_2)\,\mathbf{t}_2 - r\tau_2\mathbf{t}_1\,.
\end{aligned} \tag{12}$$

The second equality in each of these equations, i.e., the representation of the coordinate basis in terms of the (right-handed) orthonormal basis ($\mathbf{n}$,$\mathbf{t}_1$,$\mathbf{t}_2$) is derived in App. B. κ_1 and κ_2 are the normal curvatures of the curves q = const. and s = const., respectively. Because the geodesic curvatures of these are zero, they are identical to the total spatial curvatures. Their sign is chosen such that a protrusion has positive curvature, i.e., a sphere would have positive curvatures, opposite to the traditional definition in mathematics. τ_1 and τ_2 are the torsions of these curves, and in App. B it is shown that $\tau_1 = -\tau_2 \equiv \tau$.

Note that the basis vectors $\mathcal{E}_s$ and $\mathcal{E}_q$ are guaranteed to be orthogonal to each other only for $r = 0$, i.e., *on* the interface. It would certainly be possible to define coordinates that are orthogonal in a whole neighbourhood of the interface point under consideration, but the additional effort would not be justified by the minor simplifications afforded. What will become important in the following, however, is that $\mathcal{E}_r$ *is* orthogonal to the two other basis vectors. Moreover, $\mathcal{E}_r$ has unit length for all values of r, while the lengths of the two other basis vectors vary off the interface (i.e., for $r \neq 0$).

For many of the calculations to follow it is convenient to stick to the nonnormalized coordinate basis most of the time and to use the orthonormal basis only at the very end, when the dependence on simply interpretable quantities such as the curvatures is to be exhibited. This enables rather compact representations of most expressions. From (12), we first obtain the metric coefficients $g_{\alpha\beta} = \mathcal{E}_\alpha\mathcal{E}_\beta$, where $\alpha,\beta \in \{r,s,q\}$. The metric tensor then reads

$$\begin{aligned}
\left(g_{\alpha\beta}\right) &= \mathbf{g} \\
&= \begin{pmatrix} 1 & 0 & 0 \\ 0 & (1+r\kappa_1)^2 + r^2\tau^2 & 2r\tau + r^2(\kappa_1+\kappa_2)\tau \\ 0 & 2r\tau + r^2(\kappa_1+\kappa_2)\tau & (1+r\kappa_2)^2 + r^2\tau^2 \end{pmatrix},
\end{aligned} \tag{13}$$

its determinant is

$$g \equiv \det\mathbf{g} = \left[(1+r\kappa_1)(1+r\kappa_2) - r^2\tau^2\right]^2\,, \tag{14}$$

and the contravariant components of the metric tensor are obtained as

$$\begin{aligned}
\left(g^{\alpha\beta}\right) &= \mathbf{g}^{-1} \\
&= \frac{1}{g}\begin{pmatrix} g & 0 & 0 \\ 0 & (1+r\kappa_2)^2 + r^2\tau^2 & -2r\tau - r^2(\kappa_1+\kappa_2)\tau \\ 0 & -2r\tau - r^2(\kappa_1+\kappa_2)\tau & (1+r\kappa_1)^2 + r^2\tau^2 \end{pmatrix}.
\end{aligned} \tag{15}$$

From now on, we use the Einstein summation convention for pairs of covariant and contravariant indices. The vectors of the reciprocal basis are obtained from $\mathcal{E}^\alpha = g^{\alpha\beta}\mathcal{E}_\beta$:

$$\begin{aligned}
\mathcal{E}^r &= \nabla r = \mathbf{n}(s,q)\,, \\
\mathcal{E}^s &= \nabla s = \frac{1}{\sqrt{g}}\left((1+r\kappa_2)\,\mathbf{t}_1 - r\tau\mathbf{t}_2\right)\,, \\
\mathcal{E}^q &= \nabla q = \frac{1}{\sqrt{g}}\left((1+r\kappa_1)\,\mathbf{t}_2 - r\tau\mathbf{t}_1\right)\,.
\end{aligned} \tag{16}$$

The gradient and divergence read

$$\nabla = \mathcal{E}^\alpha\partial_\alpha\,, \tag{17}$$

$$\nabla\cdot\mathbf{A} = \frac{1}{\sqrt{g}}\partial_\alpha\left(\sqrt{g}g^{\alpha\beta}A_\beta\right)\,. \tag{18}$$

In the following, we will denote inner quantities by the uppercase letter corresponding to the lowercase letter denoting the outer quantity, whenever this is meaningful.

Since the interface will move in general and the coordinates r, s, q are defined with respect to the interface, there is also a transformation rule for the time derivative:

$$\partial_t f(x,y,z,t) = \partial_t F(r,s,q,t) - \mathbf{v}\nabla F(r,s,q,t)\,, \tag{19}$$

where $\mathbf{v}(s,q,t)$ is the interface velocity. Equation (19) exhibits that the time derivative in the comoving frame is a material derivative. In order to formulate the matching conditions concisely, we will occasionally also write the outer fields as functions of the variables r, s, and q (without changing their naming letter, thus in this case adhering to the physicists' convention of using a letter for a physical quantity rather than a mathematical function).

B. Inner equations

To render the scales of the different terms more visible, we rewrite Eqs. (17) and (18) in the (still exact) form

$$\nabla = \frac{1}{\epsilon}\,\mathbf{n}\,\partial_\rho + \mathcal{E}^{\bar\alpha}\partial_{\bar\alpha}\,, \tag{20}$$

$$\nabla\cdot\mathbf{A} = \frac{1}{\sqrt{g}}\left(\frac{1}{\epsilon}\,\partial_\rho\,\sqrt{g}A_r + \partial_{\bar\alpha}\,\sqrt{g}g^{\bar\alpha\bar\beta}A_{\bar\beta}\right)\,, \tag{21}$$

where sub- and superscripts carrying an overbar are taken from the set $\{s,q\}$ only in the summation.

Assuming, without loss of generality, that the tangential velocity of the interface vanishes, Eq. (10) takes the following form

$$\begin{aligned}
\partial_t\Phi - \frac{1}{\epsilon}v_n\partial_\rho\Phi &= \nabla\cdot M\nabla\frac{1}{\epsilon^2}\,\delta\mu(\nabla^2\Phi,\Phi)\,,\\
\delta\mu(\nabla^2\Phi,\Phi) &= -\frac{1}{\sqrt{g}}\,\partial_\rho\,\sqrt{g}\,\partial_\rho\Phi\\
&\quad -\epsilon^2\frac{1}{\sqrt{g}}\,\partial_{\bar\alpha}\,\sqrt{g}g^{\bar\alpha\bar\beta}\partial_{\bar\beta}\Phi\\
&\quad +2f'(\Phi) + \frac{\epsilon}{3\gamma}h'(\Phi)V_{\rm el}\,,
\end{aligned} \tag{22}$$

with

$$\nabla\cdot M\nabla = \frac{1}{\epsilon^2}\frac{1}{\sqrt{g}}\partial_\rho\,\sqrt{g}M\partial_\rho + \frac{1}{\sqrt{g}}\partial_{\bar\alpha}\,\sqrt{g}g^{\bar\alpha\bar\beta}M\partial_{\bar\beta}\,. \tag{23}$$

Hence, the leading term of the inner equation (22) with the differential operator given by (23) is of order ϵ^{-4}.

The mechanical equilibrium condition (9) becomes

$$\begin{aligned}
\nabla\tilde\Sigma &= \frac{1}{\sqrt{g}}\left(\frac{1}{\epsilon}\,\partial_\rho\,\sqrt{g}\,\tilde\Sigma_{\gamma r}\mathcal{E}^\gamma\right.\\
&\quad \left. +\,\partial_{\bar\alpha}\,\sqrt{g}\,g^{\bar\alpha\bar\beta}\tilde\Sigma_{\gamma\bar\beta}\mathcal{E}^\gamma\right) = 0\,.
\end{aligned} \tag{24}$$

C. Expansions, matched asymptotic analysis

To solve the outer and inner equations successively, we expand the fields in both the outer and inner domains in powers of ϵ

$$\begin{aligned}
\phi(x,y,z,t) &= \phi^{(0)}(x,y,z,t) + \epsilon\,\phi^{(1)}(x,y,z,t)\\
&\quad + \epsilon^2\phi^{(2)}(x,y,z,t)\ldots\,,
\end{aligned} \tag{25}$$

$$\begin{aligned}
u_{ij}(x,y,z,t) &= u_{ij}^{(0)}(x,y,z,t) + \epsilon u_{ij}^{(1)}(x,y,z,t)\\
&\quad + \epsilon^2 u_{ij}^{(2)}(x,y,z,t)\ldots\,,
\end{aligned} \tag{26}$$

and

$$\begin{aligned}
\Phi(r,s,q,t) &= \Phi^{(0)}(r,s,q,t) + \epsilon\,\Phi^{(1)}(r,s,q,t)\\
&\quad + \epsilon^2\Phi^{(2)}(r,s,q,t)\ldots\,,
\end{aligned} \tag{27}$$

$$\begin{aligned}
U_{\alpha\beta}(r,s,q,t) &= U_{\alpha\beta}^{(0)}(r,s,q,t) + \epsilon U_{\alpha\beta}^{(1)}(r,s,q,t)\\
&\quad + \epsilon^2 U_{\alpha\beta}^{(2)}(r,s,q,t)\ldots\,.
\end{aligned} \tag{28}$$

The transformation from cartesian tensor components (subscripts i, j) to curvilinear ones (sub- and superscripts α,β) is carried out using standard rules of tensor calculus. Details can be found in App. C. From the expansions of the strain fields, similar expansions (not written out here) follow for the stress fields. Moreover, the basic field variables for which the elastic equations, the Lamé equations, ultimately constitute a closed set, are the displacement vectors u_i or U_α. A peculiarity of phase-field formulations of elasticity is then that the fields $U_\alpha^{(0)}$ are independent of ρ [16], i.e., continuous across the interface, because components of the strain tensor contain derivatives $\partial_\rho U_\alpha/\epsilon$, but their leading order is ϵ^0, not ϵ^{-1}. Again, details are presented in App. C.

The asymptotic analysis of the model may be divided into two natural subproblems: analysis of the equation for the phase field and analysis of the mechanical equations; the latter depend on the former only via the solution for the phase field. Since the focus of this article is on how to capture surface diffusion dynamics correctly, only the first subproblem will be treated in the main text, a strategy that will hopefully facilitate the application of the results to other models, such as phase-field simulations of electromigration, for which they should possess relevance, too. The derivation of the sharp-interface limit of the mechanical equations is a straightforward extension of the two-dimensional case, albeit with one or two additional subtle points. Because the three-dimensional case does not seem to have been discussed in the literature before, this is done in App. C. Another motivation to carry this part of the analysis out explicitly is to present, as a case in point, an operational phase-field model for a complete physical system.

1. *Leading order*

The leading-order outer equation for ϕ is

$$\nabla\cdot M\nabla f'(\phi^{(0)}) = 0\,, \tag{29}$$

which is to be supplemented with the boundary conditions $\phi^{(0)} = 1$ and $\phi^{(0)} = 0$ at infinity in the regions where the system is solid and non-solid, respectively. If we regard (29) as a partial differential equation for the function $f'(\phi^{(0)})$ (rather than for $\phi^{(0)}$ itself), this boundary condition translates into $f'(\phi^{(0)}) \to 0$ as $|\mathbf{r}| \to \infty$, which may be seen immediately from the explicit form of $f'(\phi)$, given in App. D. The new boundary condition is valid everywhere at infinity except possibly in a region with size of order ϵ. For general $M(\phi,\epsilon\nabla\phi)$, the partial differential equation (29) is of course nonlinear. Nevertheless, it can be shown to have the unique solution $f'(\phi^{(0)}) = 0$, if M is positive everywhere, except possibly on a set of measure zero.

To see this, multiply Eq. (29) by $f'(\phi^{(0)})$, integrate over all of space and use Gauss's theorem:

$$\begin{aligned}
0 &= \int d^3x\, f'(\phi^{(0)})\nabla\cdot M\nabla f'(\phi^{(0)})\\
&= -\int d^3x M\left[\nabla f'(\phi^{(0)})\right]^2 + O(\epsilon)\,,
\end{aligned} \tag{30}$$

where the $O(\epsilon)$ stands for the surface integral at infinity. If M is positive almost everywhere, we immediately get $f'(\phi^{(0)}) =$ const., and the boundary conditions require the constant to be zero. This conclusion remains of course unchanged, if M becomes zero only when $\phi^{(0)}$ is zero or one – a standard choice [24] is $M(\phi) \propto \phi^2(1-\phi)^2$.

Hence, the unique solution to the leading-order outer problem is, if we now consider it an equation for $\phi^{(0)}$ again, $\phi^{(0)} = 1$ in Ω^- and $\phi^{(0)} = 0$ in Ω^+, where $\Omega^\mp$ are those regions of space, separated by the interface(s), in which $\lim_{|\mathbf{r}|\to\infty} \phi^{(0)} = 1$ and 0, respectively. The solution $\phi^{(0)} = \frac{1}{2}$, still possible for the equation interpreted as an equation for $f'(\phi^{(0)})$, is excluded by the boundary conditions for $\phi^{(0)}$. (This argument presupposes that we have no domains that are not connected with infinity. For the interior of a closed interface, the solution $\phi^{(0)} = 1/2$ would have to be excluded by a stability argument or by making reference to initial conditions.)

It is then seen by inspection that the outer equation is indeed solved to *all* orders by the solution under discussion (because $h'(0) = h'(1) = 0$). Therefore, we have $\phi^{(1)} \equiv 0$, $\phi^{(2)} \equiv 0$, which provides us with partial boundary conditions for the inner solutions $\Phi^{(1)}$, $\Phi^{(2)}$, and so on (see App. A). Moreover, only the inner problem needs to be considered beyond the leading order.

Because $g = 1 + O(\epsilon)$, the leading-order inner problem becomes [see Eqs. (22) and (23)]

$$\partial_\rho M(\Phi^{(0)}) \partial_\rho \left[\partial_{\rho\rho}\Phi^{(0)} - 2f'(\Phi^{(0)})\right] = 0\,, \tag{31}$$

which can be integrated once to yield

$$\partial_\rho \left[\partial_{\rho\rho}\Phi^{(0)} - 2f'(\Phi^{(0)})\right] = \frac{c_1(s,q)}{M(\Phi^{(0)})}\,, \tag{32}$$

where $c_1(s,q)$ is a function of integration. It is here that we have to follow different lines of arguments, depending on whether M approaches zero for $\rho \to \pm\infty$, which is the case for the mobilities assumed in [22, 24], or whether it is just a bounded (and possibly constant) function of ϕ. In the first case, we may immediately conclude $c_1 = 0$, because the right hand side of (32) must not diverge. In the second case, we obtain the same result by integrating (32) first and invoking the boundary conditions:

$$\partial_{\rho\rho}\Phi^{(0)} - 2f'(\Phi^{(0)}) = c_1(s,q)\int_0^\rho \frac{1}{M} d\rho + c_2(s,q)\,. \tag{33}$$

Since M is bounded from above and positive, the integral will be larger in magnitude than $\int_0^\rho 1/(\sup_\rho M) d\rho = \rho/\sup_\rho M$, so the two terms on the right hand side of Eq. (33) are linearly independent. The left hand side approaches zero for $\rho \to \pm\infty$ [the argument will be made more rigorous below in the discussion of $\Phi^{(1)}$], so both c_1 and c_2 must be equal to zero. To argue that c_2 is zero in the case where $M \to 0$ for $\rho \to \pm\infty$, we can proceed the same way, except that we have already gotten rid of the term containing c_1, so the right hand side of (33) is c_2 only.

To summarize, the leading-order inner equation results in

$$\partial_{\rho\rho}\Phi^{(0)} - 2f'(\Phi^{(0)}) = 0\,, \tag{34}$$

and this provides us with the solution $\Phi^{(0)} = {}^1\!/_2\,(1 - \tanh\rho)$ as is shown in App. D.

2. *Next-to-leading order*

The next-to-leading order in Eq. (22) is the order ϵ^{-3}. Since the differential operator in front of the chemical potential is of order ϵ^{-2} and the chemical potential multiplied by another factor ϵ^{-2}, we must expand $\delta\mu$ up to order ϵ. Equation (34) already tells us that $\delta\mu^{(0)} = 0$, so we obtain

$$\partial_\rho M(\Phi^{(0)}) \partial_\rho \delta\mu^{(1)} = 0\,, \tag{35}$$

from which we get

$$\partial_\rho \delta\mu^{(1)} = \frac{d_1(s,q)}{M(\Phi^{(0)})}\,. \tag{36}$$

As before, we can immediately conclude from this that $d_1 = 0$, if we assume $M(\Phi^{(0)}) \to 0$ for $\Phi^{(0)} \to 0, 1$. For arbitrary but bounded M, we invoke the matching conditions (see App. A)

$$\lim_{\rho\to\pm\infty} \partial_\rho \delta\mu^{(1)} = \partial_r \delta\mu^{(0)}_{\text{out}}|_{\pm 0} = 0 \tag{37}$$

to obtain the same result (where for once we have denoted an outer quantity by a subscript "out")

Integrating once more with respect to ρ and writing out $\delta\mu^{(1)}$, we have

$$\begin{aligned}\delta\mu^{(1)} \;=\; & -\partial_{\rho\rho}\Phi^{(1)} - (\kappa_1+\kappa_2)\partial_\rho\Phi^{(0)} \\ & + 2f''(\Phi^{(0)})\,\Phi^{(1)} + \frac{1}{3\gamma}h'(\Phi^{(0)})V_{\text{el}}^{(0)} = d_2(s,q)\,.\end{aligned} \tag{38}$$

Up to this point, there is agreement between this and preceding asymptotic analyses [23], if not in all details of the procedure, so at least in the results (assuming the appropriate replacement of the interaction with the electric field in the electromigration system by that with elastic strain and simplifying our result to the two-dimensional case).

Let us now try to determine the function of integration $d_2(s,q)$. A priori, there is no reason to use a procedure different from what we have done before. We know the limiting values for $\rho \to \pm\infty$ for three of the five terms on the right hand side of (38): $\lim_{\rho\to\pm\infty} \partial_\rho\Phi^{(0)} = 0$ [which follows from either the matching conditions or by inspection of the solution (D8)], $\lim_{\rho\to\pm\infty} h'(\Phi^{(0)}) = 0$ [because $h'(0) = h'(1) = 0$], $\lim_{\rho\to\pm\infty} d_2(s,q) = d_2(s,q)$ (because d_2 is independent of ρ). Moreover, from the matching conditions, we obtain the limit for $\Phi^{(1)}$

$$\begin{aligned}\Phi^{(1)} \sim \rho\phi'^{(0)}(\pm 0) + \phi^{(1)}(\pm 0) \;&=\; \phi^{(1)}(\pm 0) = 0 \\ &\qquad (\rho \to \pm\infty)\,.\end{aligned} \tag{39}$$

The second equality follows from the fact that $\phi^{(0)} = 0$ or $\phi^{(0)} = 1$, hence its derivative with respect to r vanishes on both sides of the interface; the third equality is a consequence

of the fact that $\phi^{(0)}$ solves the outer equation to all orders and hence $\phi^{(1)} \equiv 0$.

With four of the five terms in (38) having a definite limit, we may conclude that the fifth must have a limit as well and obtain

$$\lim_{\rho\to\pm\infty} -\partial_{\rho\rho}\Phi^{(1)} = d_2(s,q)\,. \tag{40}$$

But if this limit exists, it cannot be different from zero: transforming to $\xi = 1/\rho$, we see that $\partial_{\rho\rho}\Phi^{(1)} = (\xi^2\partial_\xi)^2\Phi^{(1)}$, which implies the asymptotic behaviour $\Phi^{(1)} \sim -d_2/2\xi^2$ ($\xi \to 0$) and hence the divergence of $\Phi^{(1)}$ as $-d_2\rho^2/2$, if $d_2 \neq 0$. (The same kind of argument can be used to show that the left hand side of Eq. (33) goes to zero, even though the matching conditions do not provide a direct expression for $\lim_{\rho\to\pm\infty}\partial_{\rho\rho}\Phi^{(0)}$.)

The upshot of these detailed considerations is that

$$d_2(s,q) = 0 \quad \Rightarrow \quad \delta\mu^{(1)} = 0. \tag{41}$$

Previous treatments of the problem did not enter into these considerations. Instead, one of the two following equivalent approaches was chosen. Either, Eq. (38) was interpreted as a linear inhomogeneous differential equation for $\Phi^{(1)}$ and Fredholm's alternative invoked. Since the appearing linear operator

$$\mathcal{L} = \partial_{\rho\rho} - 2f''(\Phi^{(0)}) \tag{42}$$

is hermitean, we know (from taking the derivative of Eq. (34) w.r.t. ρ) that $\partial_\rho\Phi^{(0)}$ is a solution to the adjoint homogeneous equation. The inhomogeneity of the differential equation must be orthogonal to this solution. Or else, Fredholm's alternative was not mentioned, the equation was simply multiplied by $\partial_\rho\Phi^{(0)}$, integrated, and it was shown via integration by parts that the terms containing $\Phi^{(1)}$ disappear. Of course, this is the same thing.

To exploit the approach optimally, we use the relationship $\partial_\rho\Phi^{(0)} = -h'(\Phi^{(0)})/3$ shown in App. D. This way we obtain from (38)

$$\begin{aligned} &-\int_{-\infty}^{\infty}\left[\kappa_1+\kappa_2+\frac{1}{\gamma}V_{\rm el}^{(0)}\right]\left(\partial_\rho\Phi^{(0)}\right)^2 d\rho \\ &= \int_{-\infty}^{\infty}\partial_\rho\Phi^{(0)}d_2(s,q)d\rho = -d_2(s,q) \end{aligned} \tag{43}$$

or

$$d_2(s,q) = \frac{1}{3}\left(\kappa_1+\kappa_2+\overline{V}_{\rm el}^{(0)}/\gamma\right)\,, \tag{44}$$

where we have used (D10) and introduced $\overline{V}_{\rm el}^{(0)} = \int_{-\infty}^{\infty} V_{\rm el}^{(0)}\left(\partial_\rho\Phi^{(0)}\right)^2 d\rho / \int_{-\infty}^{\infty}\left(\partial_\rho\Phi^{(0)}\right)^2 d\rho$.

Both Eqs. (41) and (44) were derived by valid methods, therefore they should both hold true. Nevertheless, as we shall see shortly, Eq. (41) is a quite undesirable result. This may be the deeper reason why it was so far overlooked and only the analog of Eq. (44) derived. When Eq. (41) is inserted in (44) it imposes a relationship between the elastic state of the material (represented by $\overline{V}_{\rm el}^{(0)}$) and the curvature. (In models, where the interaction term is quadratic in ϵ [23], it would even impose the restriction $\kappa_1 + \kappa_2 = 0$.)

3. Higher orders

To see that the model would indeed work if we did not have the restriction (41), let us consider the equations at the next two orders, ignoring for the time being the result $d_2 = 0$. Since both $\delta\mu^{(0)}(= 0)$ and $\delta\mu^{(1)}$ are independent of ρ, the first term of the operator (23) does not produce any contribution from these terms in (22), and the order ϵ^{-2} equation reads

$$\partial_\rho M\partial_\rho\delta\mu^{(2)} + \partial_{\bar\alpha}g^{\bar\alpha\bar\beta}M\partial_{\bar\beta}\delta\mu^{(0)} = 0\,, \tag{45}$$

where we can immediately drop the second term, because of $\delta\mu^{(0)} = 0$. After two integrations this becomes

$$\delta\mu^{(2)} = e_1(s,q)\int_0^\rho \frac{1}{M}d\rho + e_2(s,q)\ . \tag{46}$$

If $M \to 0$ for $\rho \to \pm\infty$, we immediately find $e_1(s,q) = 0$. In the general case, we use the matching conditions [see (A6)]

$$\begin{aligned} \delta\mu^{(2)} \ \sim\ & \frac{1}{2}\rho^2\,\partial_{rr}\delta\mu_{\rm out}^{(0)}|_{r=\pm0} + \rho\,\partial_r\delta\mu_{\rm out}^{(1)}|_{r=\pm0} \\ & + \delta\mu_{\rm out}^{(2)}|_{r=\pm0}\,. \end{aligned} \tag{47}$$

From Eq. (10), we gather that an expansion of $\delta\mu_{\rm out}$ in powers of ϵ will contain three types of terms, the first of which have the form $\nabla^2\phi^{(k)}$ ($k = 0, 1, \dots$), while the second contain factors $\phi^{(k)}$ ($k = 1, 2, \dots$), coming from an expansion of $f'(\phi)$ or $h'(\phi)$ about $\phi^{(0)}$, and the third include either $f'(\phi^{(0)})$ or $h'(\phi^{(0)})V_{\rm el}^{(k)}$ ($k = 0, 1, \dots$). All of these terms vanish, because $\phi^{(k)} = 0$ for $k > 0$ and because $f'(\phi^{(0)}) = h'(\phi^{(0)}) = 0$. This is simply a consequence of the fact that the outer equation is solved exactly by $\phi^{(0)} = 0$ and $\phi^{(0)} = 1$. The "chemical potential" appearing in the phase-field equations needs to be related to the true, i.e., sharp-interface chemical potential only at the interface. In the outer domain, it is zero. We can then conclude from (47) that $e_1(s,q) = 0$ (of course $e_2(s,q) = 0$, too, but we shall not make use of this result).

Given that $\delta\mu^{(2)}$ is independent of ρ, the inner equation at order ϵ^{-1} takes the form

$$-v_n\partial_\rho\Phi^{(0)} = \partial_\rho M\partial_\rho\delta\mu^{(3)} + \partial_{\bar\alpha}g^{\bar\alpha\bar\beta}M\partial_{\bar\beta}\,\delta\mu^{(1)}\,. \tag{48}$$

Because the surface metric $g^{\bar\alpha\bar\beta} = \delta_{\bar\alpha\bar\beta}$ to lowest order in ϵ, we find after integration over ρ (v_n does not depend on ρ)

$$\begin{aligned} v_n \ =\ & \left(\partial_{ss}+\partial_{qq}\right)\delta\mu^{(1)}\int_{-\infty}^{\infty}M(\Phi^{(0)})d\rho \\ & + M(\Phi^{(0)})\partial_\rho\delta\mu^{(3)}|_{-\infty}^{\infty}\,. \end{aligned} \tag{49}$$

Here we can drop the second term on the right hand side, if $\lim_{\rho\to\pm\infty}M(\Phi^{(0)}) = 0$. Formally setting $\int_{-\infty}^{\infty}M(\Phi^{(0)})d\rho = 3M^*\gamma$ and using (44), we arrive at

$$v_n = M^*\left(\partial_{ss}+\partial_{qq}\right)\left[\gamma(\kappa_1+\kappa_2)+\overline{V}_{\rm el}^{(0)}\right]\,. \tag{50}$$

It is shown in App. C that $\overline{V}_{\rm el}^{(0)}$ is the correct sharp-interface limit of the elastic part of the chemical potential in Eq. (1),

hence (50) reproduces the sharp-interface limit (6), as the surface Laplacian in geodesic orthogonal coordinates is given by

$$\Delta_s = \partial_{ss} + \partial_{qq} \, . \tag{51}$$

Finally, M^* would be infinite for positive functions $M(\Phi^{(0)})$ that do not reduce to zero for $\rho \to \pm\infty$; therefore, in the end we would indeed have to require $M(\Phi^{(0)})$ to decay far from the interface, if $\delta\mu^{(1)}$ were different from zero. In reality, we do not just have (50), the equation we want, but in addition Eq. (41), requiring $\delta\mu^{(1)} = 0$ and, consequently

$$v_n = 0 \, . \tag{52}$$

Thus we are led to the conclusion that the asymptotics of the phase-field model produces the correct sharp-interface limit *only at equilibrium*, i.e., when the normal velocity vanishes. Of course, one may ask what will happen, if we prepare the system in an initial state, where Eq. (10) requires the phase field to change. Then v_n will necessarily be different from zero. The answer is that in such a case the phase field will not follow its asymptotic dynamics yet. A similar phenomenon happens when a phase-field simulation is started with an initial interface perturbed by white noise. Since the asymptotics of the phase-field equations require curvatures to be smaller than $1/\epsilon$, the initial stage of the dynamics where larger curvatures are present, will not be governed by these asymptotics. But the asymptotic behaviour is sufficiently robust to keep that initial stage short. It is tempting to speculate that when conditions are such that (52) does not hold yet, the phase-field model discussed here will satisfy all less restrictive conditions such as (50) already. Then the model would be applicable during the period where the influence of condition (41) leading to (52) is still small. However, it should be clear that without a theoretical estimate of the error in this not fully asymptotic state, the model can hardly be considered quantitative. Condition (41) should be expected to have a stabilizing influence on the interface, rendering growth of instabilities less rapid than in the sharp-interface model.

At first sight, the deep quench case considered in [22] seems to escape an analogical consequence, because there the matching procedure is performed on a finite ρ domain and hence an argument leading to the restriction (41) appears to be missing. Indeed, instead of $f(\phi)$ the model has a quadratic potential $\tilde{f}(\phi) = (1-\phi^2)/2$, leading to sinusoidal behaviour of $\Phi^{(0)}$, which takes its limiting values -1 and 1 for finite ρ ($= \pm\pi/2$) already. However, closer inspection shows that the problem has not disappeared, it just takes a hidden form. The phase field must be specified beyond the domain of thickness $r = O(\epsilon)$ where $\tilde{f}(\phi) \neq 0$, which means that the definitions of $\tilde{f}'(\Phi^{(0)})$ ($= -\Phi^{(0)}$) and $\tilde{f}''(\Phi^{(0)})$ ($= -1$) have to be extended to include the values $\Phi^{(0)} = \pm 1$ into their domain. To keep Eq. (3.10b) of [22] valid for arbitrarily large ρ, it is necessary to set $\tilde{f}'(\pm 1) = 0$, i.e., to impose jump discontinuities of size 1 at the ends of the $\Phi^{(0)}$ interval [-1,1]. This is evident, as the stationary values of the phase field should correspond to minima of the potential. However, Eq. (3.13b) of [22] then becomes

$$\mu(s,t) = -\Phi^{(1)}_{\rho\rho} - \kappa\Phi^{(0)}_{\rho} + \tilde{f}''(\Phi^{(0)})\,\Phi^{(1)} \, , \tag{53}$$

where the behaviour of the second derivative of the potential is essentially given by $\tilde{f}''(\Phi^{(0)}) = -1 + \delta(\Phi^{(0)}-1) + \delta(\Phi^{(0)}+1)$. In any case, with $\tilde{f}'(\Phi^{(0)})$ exhibiting only jump discontinuies, $\tilde{f}''(\Phi^{(0)})$ cannot have stronger singularities than δ functions. The last term in Eq. (53) then becomes zero for $|\rho| > \pi/2$, because $\Phi^{(1)}$ approaches zero continuously for $\rho \to \pm\pi/2$ (and is identically 0 for $|\rho| > \pi/2$). Then the total right hand side of the equation will approach zero for $\rho \to \pm\infty$, again forcing the chemical potential $\mu(s,t)$ to be equal to zero.

It is instructive to note why the nonconservative model obtained when (10) is replaced with (7) does *not* suffer from a similar difficulty. In that model, the velocity is already determined at the next-to leading order. Instead of (38), we get

$$\begin{aligned} -v_n\partial_\rho\Phi^{(0)} \;=\; & \frac{k_v\gamma}{\rho_s}\Big\{\partial_{\rho\rho}\Phi^{(1)} + (\kappa_1+\kappa_2)\partial_\rho\Phi^{(0)} \\ & - 2f''(\Phi^{(0)})\,\Phi^{(1)} - \frac{1}{3\gamma}h'(\Phi^{(0)})V^{(0)}_{\rm el}\Big\} \, . \end{aligned} \tag{54}$$

Again we may conclude that all the terms on the right hand side go to zero as ρ is sent to $\pm\infty$. However, this does not lead to any constraints, since the left hand side is ρ dependent now and goes to zero as well, satisfying the limit automatically, whereas in the surface-diffusion case, it was a function of s and q only (d_2) that could be concluded to be equal to zero. So consideration of the limit does not produce anything new here, and the only procedure available to extract information on v_n is to use Fredholm's alternative which gives the correct sharp-interface limit.

In the case of the nonconservative model, the introduced chemical potential functional is zero in the bulk just as in the conservative case, but there are no restrictions on its variation near the interface, where it acquires a form tending to a δ function in the sharp-interface limit. In the conservative model, this is excluded by restrictions on the derivative of the chemical potential with respect to ρ, meaning that the latter must be smooth across the interface. Since it is zero off the interface, it is zero on it as well. Due to this reason, the phase-field model strictly speaking applies only to the equilibrium limit. Far-from equilibrium dynamics is not likely to be captured faithfully.

IV. TENSORIAL MOBILITY

That the phase-field model given by Eqs. (8) through (10) does not quite yield the correct asymptotics may be traced back to the fact that the differential operator $\nabla\cdot M\nabla$, prepended to the chemical potential in (10), does not reduce to the surface Laplacian Δ_s in the asymptotic limit. In fact, the second term on the right hand side of Eq. (23) *is* the Laplace-Beltrami operator on the surface, but the first term, containing derivatives with respect to ρ is orders of magnitude larger, being preceded by a factor of $1/\epsilon^2$. As a consequence, the asymptotics must be secured by the full solution of the equation rather than by both the operator and the chemical potential converging to the desired sharp-interface limits.

Realizing this property of the model, it seems natural to modify the differential operator via introduction of an essentially tensorial mobility. Let us denote by

$$\hat{\mathbf{n}} = -\frac{\nabla\phi}{|\nabla\phi|} \tag{55}$$

the normal on the surface $\phi = $ const. (for $\phi = 1/2$, we have $\hat{\mathbf{n}} = \mathbf{n}$), then we expect the operator

$$\nabla \cdot (1 - \hat{\mathbf{n}} : \hat{\mathbf{n}})\, \nabla \tag{56}$$

to reduce to the surface Laplacian asymptotically. A colon is used to designate a dyadic product, so $1 - \hat{\mathbf{n}} : \hat{\mathbf{n}}$ is a projection operator projecting onto the tangential plane of a level set of ϕ. Introducing the shorthand $\phi_{,\alpha} = \partial_\alpha \phi$, we have $\nabla\phi = \mathcal{E}^\alpha \phi_{,\alpha}$ and

$$\begin{aligned}\nabla\cdot (1 - \hat{\mathbf{n}} : \hat{\mathbf{n}})\, \nabla = \\ \nabla \cdot \left(\mathcal{E}^\mu \partial_\mu - \frac{1}{(\nabla\phi)^2} \mathcal{E}^\alpha \phi_{,\alpha}\, g^{\beta\mu} \phi_{,\beta}\, \partial_\mu \right) = \\ \frac{1}{\sqrt{g}} \partial_\nu \sqrt{g} g^{\nu\mu} \left(\partial_\mu - \frac{1}{(\nabla\phi)^2} \phi_{,\mu}\, g^{\alpha\beta} \phi_{,\alpha}\, \partial_\beta \right) .\end{aligned} \tag{57}$$

The third expression is obtained from the second applying the divergence operator (18) and renaming $\alpha \to \mu, \beta \to \alpha, \mu \to \beta$ in the three pairs of "mute" indices.

To expand this operator in powers of ϵ in the inner domain, we use the fact that $g^{\rho\bar{\alpha}} = 0$ and that

$$\begin{aligned}(\nabla\Phi)^2 &\equiv \frac{1}{\epsilon^2} (\tilde{\nabla}\Phi)^2 , \\ (\tilde{\nabla}\Phi)^2 &= \epsilon^2 \Phi_{,\alpha}\, g^{\alpha\beta} \Phi_{,\beta} = \Phi_{,\rho}^2 + \epsilon^2 \Phi_{,\bar{\alpha}}\, g^{\bar{\alpha}\bar{\beta}} \Phi_{,\bar{\beta}} .\end{aligned} \tag{58}$$

Inserting this into (57) and carrying the expansion to formal order ϵ^0, we find first that the order ϵ^{-2} terms (containing two derivatives with respect to ρ) cancel each other. The remainder reads

$$\begin{aligned}\nabla\cdot (1 - \hat{\mathbf{n}} : \hat{\mathbf{n}})\, \nabla = \\ \frac{1}{\sqrt{g}}\, \partial_\rho \sqrt{g} \left(\frac{\Phi_{,\bar{\alpha}}\, g^{\bar{\alpha}\bar{\beta}} \Phi_{,\bar{\beta}}}{(\tilde{\nabla}\Phi)^2} \partial_\rho - \frac{\Phi_{,\rho}\, g^{\bar{\alpha}\bar{\beta}} \Phi_{,\bar{\alpha}}}{(\tilde{\nabla}\Phi)^2} \partial_{\bar{\beta}} \right) \\ + \frac{1}{\sqrt{g}}\, \partial_{\bar{\nu}} \sqrt{g} g^{\overline{\nu\mu}} \left(\partial_{\bar{\mu}} - \frac{\Phi_{,\rho}\, \Phi_{,\bar{\mu}}}{(\tilde{\nabla}\Phi)^2} \partial_\rho \right) + O(\epsilon) ,\end{aligned} \tag{59}$$

and this expression still contains derivatives with respect to ρ. However, *if* the leading-order solution $\Phi^{(0)}$ depends on ρ only, as it did in the last section, then all the derivatives of Φ with respect to s and q (i.e., with respect to the variables marked by an overbar) are $O(\epsilon)$ at least, and Eq. (59) reduces to $\nabla\cdot(1-\hat{\mathbf{n}} : \hat{\mathbf{n}})\nabla = {}^1\!/_{\sqrt{g}}\, \partial_{\bar{\nu}} \sqrt{g} g^{\nu\mu} \partial_{\bar{\mu}} + O(\epsilon)$, i.e., at leading order the operator indeed becomes the Laplace-Beltrami operator on the surface.

This then suggests to replace the phase-field equation (10) with

$$\frac{\partial\phi}{\partial t} = M \nabla \cdot (1 - \hat{\mathbf{n}} : \hat{\mathbf{n}})\, \nabla \frac{1}{\epsilon^2} \delta\mu(\nabla^2\phi, \phi) , \tag{60}$$

where $\delta\mu$ is unchanged from (10) but M is a constant mobility now.

In this model, the equation for the velocity would appear at the next-to leading order already and take the form

$$\begin{aligned}v_n \partial_\rho \Phi^{(0)} &= M \left(\partial_{ss} + \partial_{qq} \right) \Big\{ \partial_{\rho\rho} \Phi^{(1)} + (\kappa_1 + \kappa_2) \partial_\rho \Phi^{(0)} \\ &\quad - 2 f''(\Phi^{(0)})\, \Phi^{(1)} - \frac{1}{3\gamma} h'(\Phi^{(0)}) V_{\mathrm{el}}^{(0)} \Big\} .\end{aligned} \tag{61}$$

Because the operators $\mathcal{L}$ [defined in Eq. (42)] and $\partial_{ss} + \partial_{qq}$ commute, Fredholm's alternative could be applied as in the nonconservative case. This eliminates $\Phi^{(1)}$ from the equation and produces the correct sharp-interface limit.

In spite of this enjoyable state of affairs, model (60) fails much more miserably than (10). The reason is that the zeroth-order solution is not unique. In fact, the leading-order outer equation

$$\nabla \cdot \left(1 - \hat{\mathbf{n}}^{(0)} : \hat{\mathbf{n}}^{(0)} \right) \nabla f'(\phi^{(0)}) = 0 \tag{62}$$

is solved by *any* (differentiable) function $\phi^{(0)}$ satisfying the boundary conditions: obviously we have $\nabla f'(\phi^{(0)}) = f''(\phi^{(0)}) \nabla\phi^{(0)}$, whence

$$\begin{aligned}\hat{\mathbf{n}}^{(0)} : \hat{\mathbf{n}}^{(0)} \nabla f'(\phi^{(0)}) &= -\hat{\mathbf{n}}^{(0)} f''(\phi^{(0)}) |\nabla\phi^{(0)}| \\ &= f''(\phi^{(0)}) \nabla\phi^{(0)} = \nabla f'(\phi^{(0)}) ,\end{aligned} \tag{63}$$

which implies $(1 - \hat{\mathbf{n}}^{(0)} : \hat{\mathbf{n}}^{(0)}) \nabla f'(\phi^{(0)}) = 0$ for all functions f' of $\phi^{(0)}$.

It can be said that this model fails for reasons complementary to those of the scalar model. Whereas we had one equation too many in that case, adding a constraint to the desired sharp-interface dynamics, now we have one equation too few, as there is nothing in the model fixing $\phi^{(0)}$. If we had the right $\phi^{(0)}$, the tensorial model would work perfectly. In particular, it would give the limiting equations at lower order than the scalar model, which may have positive implications for the numerical cost at a given desired level of accuracy, as will be discussed in the conclusions.

V. MODEL WITH CORRECT ASYMPTOTICS - MODIFIED TENSORIAL MOBILITY

In order to obtain a model not plagued by either of the disadvantages of the two cases discussed, it appears that we have to combine ideas from both. While it is certainly desirable to have a differential operator that itself approaches the surface Laplacian, it should do so only for phase field functions that have the correct leading-order profile.

This can be achieved by modifying $1 - \hat{\mathbf{n}} : \hat{\mathbf{n}}$ into

$$Q \equiv 1 - \epsilon^2 \frac{\nabla\phi : \nabla\phi}{4 f(\phi)} = 1 - \frac{\epsilon^2 (\nabla\phi)^2}{4 f(\phi)} \hat{\mathbf{n}} : \hat{\mathbf{n}} . \tag{64}$$

If we replace the projection operator in Eq. (60) by Q, then the *outer* equation at leading order will have the same differential operator as the scalar model with constant M.

On the other hand, in the *inner* domain, we have, *provided* $\Phi^{(0)}$ solves the differential equation (D6), $\epsilon^2(\nabla\Phi)^2 = \Phi_{,\rho}^2 + O(\epsilon^2) = 4f(\Phi) + O(\epsilon)$ [this follows from Eqs. (58), (D7), and (D1)], whence $Q \approx 1 - \hat{\mathbf{n}} : \hat{\mathbf{n}}$.

This approximation is accurate up to $O(\epsilon)$ only, which is not sufficient, because the order ϵ correction would enter as a bothersome additive term in the next-to leading order inner equation.

A better inner approximation to $1 - \hat{\mathbf{n}} : \hat{\mathbf{n}}$ than just Q is provided by a minor modification. Obviously, we have $Q = 1 - \hat{\mathbf{n}} : \hat{\mathbf{n}} + O(\epsilon)\,\hat{\mathbf{n}} : \hat{\mathbf{n}}$ in the inner region. Taking this to some integer power m we get, because $1 - \hat{\mathbf{n}} : \hat{\mathbf{n}}$ and $\hat{\mathbf{n}} : \hat{\mathbf{n}}$ are orthogonal projectors:

$$Q^m = 1 - \hat{\mathbf{n}} : \hat{\mathbf{n}} + O(\epsilon^m)\,\hat{\mathbf{n}} : \hat{\mathbf{n}}\,. \tag{65}$$

These considerations lead us to make the ansatz

$$\begin{aligned} \frac{\partial\phi}{\partial t} &= M\nabla\cdot Q^m\nabla\frac{1}{\epsilon^2}\,\delta\mu(\nabla^2\phi,\phi)\,, \\ \delta\mu(\nabla^2\phi,\phi) &\equiv -\epsilon^2\nabla^2\phi + 2f'(\phi) + \frac{\epsilon}{3\gamma}h'(\phi)V_{\rm el} \end{aligned} \tag{66}$$

and leave the precise choice of the value of m for later – it will be suggested by the asymptotic analysis.

The corresponding inner equations are

$$\begin{aligned} \partial_t\Phi - \frac{1}{\epsilon}v_n\partial_\rho\Phi &= M\nabla\cdot Q^m\nabla\frac{1}{\epsilon^2}\,\delta\mu(\nabla^2\Phi,\Phi)\,, \\ \delta\mu(\nabla^2\Phi,\Phi) &= -\frac{1}{\sqrt{g}}\,\partial_\rho\sqrt{g}\,\Phi_{,\rho} \\ &\quad -\epsilon^2\frac{1}{\sqrt{g}}\,\partial_{\bar\alpha}\sqrt{g}g^{\bar\alpha\bar\beta}\Phi_{,\bar\beta} \\ &\quad +2f'(\Phi) + \frac{\epsilon}{3\gamma}h'(\Phi)V_{\rm el}\,, \end{aligned} \tag{67}$$

with

$$\begin{aligned} \nabla\cdot Q^m\nabla = &\frac{1}{\sqrt{g}}\partial_\nu\sqrt{g}g^{\nu\mu}\Big\{\partial_\mu - \Big[1 - \Big(1 - \frac{\epsilon^2(\nabla\Phi)^2}{4f(\Phi)}\Big)^m\Big] \\ &\times\frac{1}{(\nabla\Phi)^2}\Phi_{,\mu}\,g^{\alpha\beta}\Phi_{,\alpha}\,\partial_\beta\Big\}\,. \end{aligned} \tag{68}$$

A. Leading order

In the outer equations, Q becomes the identity operator to leading order, i.e., $Q^{(0)}(\phi^{(0)}) = 1$, and at the lowest order in ϵ, we have

$$\nabla^2 f'(\phi^{(0)}) = 0\,, \tag{69}$$

a Laplace equation that we know to be uniquely solvable for $f'(\phi^{(0)})$ with Dirichlet boundary conditions at infinity. This boundary condition is even homogeneous (except possibly in a boundary region of order ϵ), leading to the unique solution $f'(\phi^{(0)}) \equiv 0$. This leaves us with the three possibilities $\phi^{(0)} = 0,\ 1/2,\ 1$, of which $\phi^{(0)} = 0$ or $\phi^{(0)} = 1$ are realized, according to the particular boundary condition on $\phi^{(0)}$.

Again, $\phi = 0$ and $\phi = 1$ are solutions to the outer problem at all orders of ϵ. Admittedly, the operator Q becomes indefinite at order ϵ^2 for $\phi = 0$ and $\phi = 1$ [because of the denominator $f(\phi)$], but this does not matter, since the expression for $\delta\mu$ alone is zero already at $\phi = 0$ and $\phi = 1$.

The leading-order inner equation reads [$g = 1 + O(\epsilon)$]

$$\partial_\rho\left[1 - \frac{\big(\Phi_{,\rho}^{(0)}\big)^2}{4f(\Phi^{(0)})}\right]^m\partial_\rho\Big(\partial_{\rho\rho}\Phi^{(0)} - 2f'(\Phi^{(0)})\Big) = 0\,. \tag{70}$$

Clearly, this is solved by $\Phi^{(0)} = 1/2\,(1 - \tanh\rho)$, which makes both the expression in brackets and in large parentheses vanish. If we require m to be even, this solution is moreover unique (up to translations, which are eliminated by the requirement that the interface be at $\rho = 0$). For as soon as we assume $(\Phi_{,\rho}^{(0)})^2 \neq 4f(\Phi^{(0)})$, the mth power of the bracket expression will be positive, allowing us to use similar arguments as in Sec. III C between Eqs. (31) and (34) to prove that $\partial_{\rho\rho}\Phi^{(0)} - 2f'(\Phi^{(0)}) = 0$, and hence the bracket expression must be zero, contrary to our assumption. Thus we do get a definite solution for $\Phi^{(0)}$ from the inner equation, which moreover shows that at leading order of the inner expansion the second-order ρ derivatives of the operator $\nabla\cdot Q^m\nabla$ cancel each other.

B. Next-to-leading order

To simplify computations at the next order, we first expand $\nabla\cdot Q^m\nabla$ up to formal order ϵ^0. This produces

$$\begin{aligned} &\nabla\cdot Q^m\nabla = \\ &\quad\frac{1}{\sqrt{g}}\,\partial_{\bar\nu}\sqrt{g}g^{\bar\nu\bar\mu}\partial_{\bar\mu} + \frac{1}{\sqrt{g}}\,\frac{1}{\epsilon^2}\partial_\rho\sqrt{g}\left(1 - \frac{\epsilon^2(\nabla\Phi)^2}{4f(\Phi)}\right)^m\partial_\rho \\ &\quad - \frac{1}{\sqrt{g}}\,\partial_\rho\sqrt{g}\frac{1}{\Phi_{,\rho}}g^{\bar\alpha\bar\beta}\Phi_{,\bar\alpha}\,\partial_{\bar\beta} - \frac{1}{\sqrt{g}}\,\partial_{\bar\nu}\sqrt{g}\frac{1}{\Phi_{,\rho}}g^{\bar\nu\bar\mu}\Phi_{,\bar\mu}\,\partial_\rho \\ &\quad + \frac{1}{\sqrt{g}}\,\partial_\rho\sqrt{g}\frac{1}{\Phi_{,\rho}^2}\Phi_{,\bar\alpha}\,g^{\bar\alpha\bar\beta}\Phi_{,\bar\beta}\,\partial_\rho + O(\epsilon)\,, \end{aligned} \tag{71}$$

Given that $\Phi^{(0)}$ is a function of ρ only, we realize that the third and fourth terms on the right hand side are $O(\epsilon)$, containing derivatives with respect to s or q of Φ, the fifth is even $O(\epsilon^2)$, so these terms may be dropped immediately in an expansion up to $O(1)$. The second term on the right hand side owes its existence the fact that Q is not exactly the projection operator on $\hat{\mathbf{n}}$ [note that no such term is present in Eq. (59)] and it has a prefactor of $1/\epsilon^2$ due to the double derivative in ρ. This term which is desirable at leading order, because without it we would not have a determinate zeroth order solution $\Phi^{(0)}$, is somewhat disturbing at the next order. Since the order of this term is $O(\epsilon^{m-2})$, we can make it small by choosing $m \geq 3$, i.e., restricting ourselves to even m for the reasons discussed before, we set $m = 4$. Then the only remaining term on the right hand side of Eq. (71) up to order ϵ^0 is the first term, which is the desired surface Laplacian.

Using this result, we can write the next-to-leading (nontrivial) order inner equation

$$\begin{aligned} -v_n\partial_\rho\Phi^{(0)} &= M\frac{1}{\sqrt{g}}\,\partial_{\bar\nu}\sqrt{g}g^{\overline{\nu\mu}}\partial_{\bar\mu}\delta\mu^{(1)}\,, \\ \delta\mu^{(1)} &= -\Big\{\mathcal{L}\Phi^{(1)} + (\kappa_1+\kappa_2)\partial_\rho\Phi^{(0)} \\ &\qquad - \frac{1}{3\gamma}h'(\Phi^{(0)})V_{\mathrm{el}}^{(0)}\Big\}\,, \end{aligned} \tag{72}$$

again with $\mathcal{L}$ as given in Eq. (42).

Note that we actually seem to have skipped orders here. The leading-order inner equation is formally $O(\epsilon^{-4})$, but once the zeroth-order inner solution is fixed, the differential operator $\nabla\cdot Q^m\nabla$ is, according to (71), of order $\epsilon^{\max(0,m-2)}$ only, so the order ϵ^{-3} vanishes identically. The order ϵ^{-2} is satisfied automatically, because the zeroth-order chemical potential is zero; the next nontrivial order is ϵ^{-1}. Alternatively, one may say that the effective leading order has become ϵ^{-2}.

Keeping only order one terms of the surface Laplacian, we have $1/\sqrt{g}\,\partial_{\bar\nu}\sqrt{g}g^{\overline{\nu\mu}}\partial_{\bar\mu} = \partial_{ss}+\partial_{qq}$, and the total linear operator in front of $\Phi^{(1)}$ becomes $-(\partial_{ss}+\partial_{qq})\mathcal{L}$. It is hermitian, because its hermitian factors commute. Hence, $\partial_\rho\Phi^{(0)}$ is a left null eigenfunction. Multiplying (72) from the left by it, integrating with respect to ρ from $-\infty$ to ∞, we obtain Eq. (50), with $M = M^*\gamma$; to arrive at Eq. (6), we have to set $M = D_s\gamma/\rho_s$. Together with App. C, this proves that the phase-field model of this section exhibiting a modified tensorial mobility has the correct asymptotic behaviour for small ϵ, neither overconstraining the system by adding, nor leaving it indeterminate by losing equations.

VI. CONCLUSIONS

The intuitive approach to constructing a phase-field model for surface diffusion consists in using the chemical potential known from the nonconservative model to define a current, involving its gradient and a mobility that vanishes in the bulk phases, and to take the divergence of this current as the time derivative of the phase field. As has been shown in this article, this approach fails to produce the correct asymptotics in a subtle way. It does reproduce the equlibrium limit correctly.

Next, the idea was explored that this failure might be remedied by making the mobility a tensor. After all, surface diffusion may be interpreted as highly anisotropic three-dimensional diffusion with a diffusion tensor that has zero eigenvalue in one direction. A straightforward realization of this idea fails in a rather drastic way, because restricting diffusion to the surfaces of constant phase field does not impose any functional dependence of ϕ in the normal direction.

A modification of the tensorial mobility however leads to a model exhibiting the correct asymptotics. This model is given by the equations (64), (66) with $m = 4$, (8), and (9). Larger even values of m also give valid models, a fact that might be useful in optimizing numerical performance. It is possible that $m = 3$ will lead to a valid model, too, but without positivity of the mobility tensor, it is difficult to prove that the inner equation (70) is solved by a unique phase-field profile.

Since the condition (52) destroying the asymptotic correctness of the scalar-mobility model is a strong restriction, it is conceivable that the model will satisfy the other equations while not being asymptotic yet and therefore keep some of its utility. It should however be emphasized that no positive assertions concerning its quantitative validity are available for this case. The problem of making reliable analytic statements about a nonasymptotic state is rather difficult.

If the scalar-mobility model had a range of quantitative validity, this would be restricted to some finite time interval, before the full asymptotics kicks in. Even then, it may be argued that the modified tensorial model discussed here is probably more useful for numerical simulations. The point is the following. In the scalar-mobility model, the inner equation determining the interface velocity appears only three orders in ϵ after the leading order. A simulation must of course represent the full model equations. Suppose we wish the interface velocity to be determined with an error not exceeding order ϵ. Then the leading-order equation must be simulated with an accuracy $O(\epsilon^4)$ at least. If one takes a simple second-order accurate discretization for the gradient operators in the equations, the numerical error due to discretization alone will be $O(a^2)$ for a grid spacing a. To keep this smaller than ϵ^4, the grid spacing would have to scale with ϵ^2, which can be expected to lead to prohibitive computation times. Therefore, in the scalar mobility model, high-accuracy discretizations would be mandatory, even if the asymptotic error were controllable.

On the other hand, in the model discussed in Sec. V, as soon as the phase-field profile is represented with an error of order ϵ or better, the effective leading order is only one order lower than the one determining the interface velocity, similar to the nonconservative case. Hence, reasonable accuracy should be attainable with grid spacings that scale as ϵ, not as ϵ^2. None of the benefits of high-accuracy discretizations would be lost to the need of representing terms very accurately that are very small in the leading-order equation.

Comparing the structure of the scalar-mobility model and the one based on a modified tensorial mobility, it is clear that the former model has much more intuitive appeal while the latter looks pretty complicated. But it has the virtue of producing the correct sharp-interface asymptotics. Very likely, in the future simpler and more elegant models will turn up doing the same thing. In the meantime, this one may be of use.

Acknowledgments Support of this work by DFG grants KA 672/5-4 and KA 672/9-1 is gratefully acknowledged.

APPENDIX A: MATCHING CONDITIONS

Let $\tilde\psi(x,y,z,t) = \psi(r,s,q,t)$ be some arbitrary (sufficiently often differentiable) function of space and time obtained in solving the outer equations. We write the corresponding function of the inner solution as $\Psi(\rho,s,q,t)$, and suppress from now on, in this section, the dependence of functions on s, q, and t. Moreover, we write the coefficient functions in expansions with respect to ϵ with simple subscripts indicating their order rather than superscripts in parentheses as in the main text. There, the notation is dictated by the fact that a subscript

would interfere with subscripts indicating tensor components; here, a superscript would interfere with the primes denoting derivatives.

We must have the asymptotic relationship

$$\Psi(\rho) \sim \psi(r) = \psi(\epsilon\rho) \quad (\rho \to \infty,\, \epsilon \to 0,\, \epsilon\rho \to 0)\,. \tag{A1}$$

Expanding both functions in powers of ϵ, we get

$$\Psi(\rho) = \Psi_0(\rho) + \epsilon\Psi_1(\rho) + \epsilon^2\Psi_2(\rho) + \dots\,, \tag{A2}$$

$$\begin{aligned}\psi(\epsilon\rho) &= \psi_0(r) + \epsilon\psi_1(r) + \epsilon^2\psi_2(r) + \dots \\ &= \psi_0(0) + \epsilon[\rho\psi_0'(0) + \psi_1(0)] \\ &\quad + \epsilon^2[\rho^2\frac{1}{2}\psi_0''(0) + \rho\psi_1'(0) + \psi_2(0)] + \dots\,,\end{aligned} \tag{A3}$$

where the derivatives are to be taken for $r \to +0$, should they be discontinuous at $r = 0$. Analogous expressions with $r \to -0$ are obtained for the asymptotics as $\rho \to -\infty$.

Equating powers of ϵ, we then successively get the asymptotic relationships

$$\lim_{\rho\to\pm\infty} \Psi_0(\rho) = \psi_0(\pm 0)\,, \tag{A4}$$

$$\Psi_1(\rho) \sim \rho\psi_0'(\pm 0) + \psi_1(\pm 0) \quad (\rho \to \pm\infty)\,, \tag{A5}$$

$$\Psi_2(\rho) \sim \frac{1}{2}\rho^2\psi_0''(\pm 0) + \rho\psi_1'(\pm 0) + \psi_2(\pm 0) \quad (\rho \to \pm\infty)\,. \tag{A6}$$

Moreover, asymptotic relations such as (A5) can be decomposed into statements about function limits

$$\lim_{\rho\to\pm\infty} \partial_\rho\Psi_1(\rho) = \psi_0'(\pm 0)\,, \tag{A7}$$

$$\lim_{\rho\to\pm\infty} \left[\Psi_1(\rho) - \rho\psi_0'(\pm 0)\right] = \psi_1(\pm 0)\,. \tag{A8}$$

APPENDIX B: LOCAL COORDINATES AND METRIC

Once the coordinates s, q on the interface have been chosen and the third coordinate r has been specified via (11), the coordinate basis (12) and, hence, the metric is determined. However, in order to obtain explicit expressions and because it is desirable to interpret the metric in terms of familiar geometric concepts, we need a few additional considerations.

For any curve $\mathbf{r} = \mathbf{R}(s)$ on a surface, an accompanying orthonormal frame can be defined consisting of the normal on the surface $\mathbf{n}$ at the considered curve point, its tangent $\mathbf{t}$, proportional to $\partial_s\mathbf{R}(s)$ (and equal to it, if s is the arclength), and the vector $\mathbf{l} = \mathbf{n} \times \mathbf{t}$. This triple, in the older German literature [27] sometimes referred to as the Bonnet-Kowalewski trihedron, is more commonly known under the name of Darboux frame [28]. It satisfies the following equations:

$$\begin{pmatrix} \partial_s\mathbf{n} \\ \partial_s\mathbf{t} \\ \partial_s\mathbf{l} \end{pmatrix} = \begin{pmatrix} 0 & \kappa & \tau \\ -\kappa & 0 & \alpha \\ -\tau & -\alpha & 0 \end{pmatrix} \begin{pmatrix} \mathbf{n} \\ \mathbf{t} \\ \mathbf{l} \end{pmatrix}, \tag{B1}$$

where κ is the normal curvature, i.e., the curvature of the projection of the curve onto the plane spanned by its tangent and the surface normal, α is the geodesic curvature, i.e., the curvature of the projection of the curve onto the tangential plane of the surface, and τ is the geodesic torsion. The total curvature κ_s of the space curve given by $\mathbf{R}(s)$ is related to the normal and geodesic curvatures via

$$\kappa_s^2 = \alpha^2 + \kappa^2\,. \tag{B2}$$

In the mathematical literature [27], the sign conventions for the normal curvature and geodesic torsion are opposite to the ones used here.

If we identify our general curve on the surface with a coordinate curve of constant q from Sec. III A, then the Darboux frame will consist of the vectors $\mathbf{n}$, $\mathbf{t}_1$, and $\mathbf{t}_2$ varying with s; if we identify it with a curve of constant s, the Darboux frame is given by $\mathbf{n}$, $\mathbf{t}_2$, and $-\mathbf{t}_1$ (it is defined right-handed). This provides us with formulas for the derivatives of the normal and tangent vectors of the surface,

$$\frac{\partial\mathbf{n}}{\partial s} = \kappa_1\mathbf{t}_1 + \tau_1\mathbf{t}_2\,, \tag{B3}$$

$$\frac{\partial\mathbf{t}_1}{\partial s} = -\kappa_1\mathbf{n} + \alpha_1\mathbf{t}_2\,, \tag{B4}$$

$$\frac{\partial\mathbf{t}_2}{\partial s} = -\tau_1\mathbf{n} - \alpha_1\mathbf{t}_1\,, \tag{B5}$$

$$\frac{\partial\mathbf{n}}{\partial q} = \kappa_2\mathbf{t}_2 - \tau_2\mathbf{t}_1\,, \tag{B6}$$

$$\frac{\partial\mathbf{t}_2}{\partial q} = -\kappa_2\mathbf{n} - \alpha_2\mathbf{t}_1\,, \tag{B7}$$

$$\frac{\partial\mathbf{t}_1}{\partial q} = \tau_2\mathbf{n} + \alpha_2\mathbf{t}_2\,, \tag{B8}$$

from which we immediately get the expressions (12) for the vectors of the canonical coordinate basis $\{\mathcal{E}_r, \mathcal{E}_s, \mathcal{E}_q\}$. Moreover, we obtain some simplifications. Because $\mathcal{E}_\alpha = \partial_\alpha\mathbf{r}$, we have the identities

$$\partial_\beta\mathcal{E}_\alpha = \partial_\alpha\mathcal{E}_\beta\,. \tag{B9}$$

These are automatically fulfilled, if $\alpha = r$ or $\beta = r$, but yield nontrivial relationships for $\alpha = s, \beta = q$.

Consider a point $\mathbf{r} = \mathbf{R}(s, q)$ on the interface. Then $\mathcal{E}_s = \partial_s\mathbf{R}(s, q) = \mathbf{t}_1$, $\mathcal{E}_q = \partial_q\mathbf{R}(s, q) = \mathbf{t}_2$, because we have specified our coordinates to be arclengths (otherwise, $\mathcal{E}_s$ and $\mathcal{E}_q$ would not be equal, just proportional to the unit tangent vectors). From (B5) and (B8), we deduce that

$$\tau_2\mathbf{n} + \alpha_2\mathbf{t}_2 = -\tau_1\mathbf{n} - \alpha_1\mathbf{t}_1\,. \tag{B10}$$

Since the tangential vectors are linearly independent this implies $\alpha_1 = \alpha_2 = 0$, i.e., the geodesic curvature vanishes and our coordinate curves are necessarily geodesics. Then their normal curvature becomes equal (up to a sign) to the spatial curvature, and formulas (B3) through (B8) reduce to the better known Frenet-Serret formulas [27, 28]. Secondly, we obtain from Eq. (B10) that $\tau_1 = -\tau_2$, because the prefactors of the normal vector must match.

This means that the metric, Eq. (13), when restricted to the interface, will depend on just three parameters, viz. κ_1, κ_2, and τ. But this is precisely the number of independent elements of a symmetric 2×2 tensor, so we can describe the most general metric this way locally.

To complete the discussion of geometric relationships near the interface, let us note that formula (18) applied to $\mathbf{A} = \mathcal{E}_r$ at $r = 0$, yields

$$\kappa \equiv \nabla\cdot\mathbf{n} = \kappa_1 + \kappa_2\,, \tag{B11}$$

i.e., the mean curvature κ is the sum of *any* two normal curvatures corresponding to orthogonal directions, not just the sum of the two principal curvatures. This is the ultimate justification for using the same notation for the principal curvatures in Sec. II and the normal curvatures in Sec. III A.

Another interesting geometric quantity is the Gaussian curvature κ_G, given as the product of the two *principal* curvatures. A general formula in terms of the Darboux frame is

$$\kappa_G = \det\left(\mathbf{n}, (\mathbf{t}_1\cdot\nabla)\mathbf{n}, (\mathbf{t}_2\cdot\nabla)\mathbf{n}\right) = \mathbf{n}\left(\partial_s\mathbf{n}\times\partial_q\mathbf{n}\right)\,. \tag{B12}$$

Evaluating this with the help of (B3) and (B6), we find an expression for the Gaussian curvature in terms of normal curvatures and torsions

$$\kappa_G = \kappa_1\kappa_2 - \tau^2\,. \tag{B13}$$

From this, one may conclude that the torsions have to vanish when κ_1 and κ_2 become the principal curvatures, i.e., take their extremal values.

APPENDIX C: SHARP-INTERFACE LIMIT OF THE ELASTIC PART OF THE MODEL

Loosely speaking, the title of this appendix refers to two things. On the one hand, it must be shown that Eq. (9) reproduces the bulk elastic equations as well as the boundary conditions for the elastic problem. On the other hand, $\bar{V}_{\rm el}^{(0)}$ must be evaluated and shown to be the elastic contribution to the chemical potential of Eq. (1).

The first task is easily accomplished. Inserting the outer solutions $\phi = 1$ and $\phi = 0$ into (9), we obtain

$$\sum_j \frac{\partial\sigma_{ij}}{\partial x_j} = 0\,, \tag{C1}$$

$$\frac{\partial p}{\partial x_i} = 0\,, \tag{C2}$$

which are the mechanical equilibrium conditions in the solid and the liquid, respectively. The boundary conditions follow from the inner equation (24), which at leading order reduces to

$$\begin{aligned} 0 &= \partial_\rho\left(\tilde{\Sigma}^{(0)}_{\gamma r}\mathcal{E}^\gamma\right) + O(\epsilon) \\ &= \mathbf{n}\partial_\rho\tilde{\Sigma}^{(0)}_{rr} + \mathbf{t}_1\partial_\rho\tilde{\Sigma}^{(0)}_{sr} + \mathbf{t}_2\partial_\rho\tilde{\Sigma}^{(0)}_{qr} + O(\epsilon)\,, \end{aligned} \tag{C3}$$

where we have used that the $\mathcal{E}^\gamma$ become the basis vectors of the Darboux frame at leading order and that these are independent of r and, hence, ρ. From (C3), we have

$$\partial_\rho\tilde{\Sigma}^{(0)}_{rr} = \partial_\rho\tilde{\Sigma}^{(0)}_{sr} = \partial_\rho\tilde{\Sigma}^{(0)}_{qr} = 0\,, \tag{C4}$$

i.e., the three appearing components of the generalized stress tensor are independent of ρ. The matching conditions then provide us with

$$\sigma_{nn} = \lim_{\rho\to-\infty}\tilde{\Sigma}^{(0)}_{rr} = \lim_{\rho\to\infty}\tilde{\Sigma}^{(0)}_{rr} = -p\,, \tag{C5}$$

$$\sigma_{nt_1} = \lim_{\rho\to-\infty}\tilde{\Sigma}^{(0)}_{rs} = \lim_{\rho\to\infty}\tilde{\Sigma}^{(0)}_{rs} = 0\,, \tag{C6}$$

$$\sigma_{nt_2} = \lim_{\rho\to-\infty}\tilde{\Sigma}^{(0)}_{rq} = \lim_{\rho\to\infty}\tilde{\Sigma}^{(0)}_{rq} = 0\,, \tag{C7}$$

with the limit values in the nonsolid phase ($\rho\to\infty$) following directly from (9). At the next order, the phase-field equations yield the capillary overpressure correction to (C5), but we shall not consider this level of detail here.

For the second task, we need the strain tensor $\mathcal{U}$ in curvilinear coordinates to evaluate (8) in the inner domain. To perform the transformation, we first note that ($\mathcal{E}^i_\alpha$ is the ith cartesian component of $\mathcal{E}_\alpha$)

$$\begin{aligned} U_{\alpha\beta} &= \mathcal{E}_\alpha\mathcal{U}\mathcal{E}_\beta = U_{ij}\mathcal{E}^i_\alpha\mathcal{E}^j_\beta \\ &= \frac{1}{2}\left(U_{i,j}+U_{j,i}\right)\frac{\partial x^i}{\partial\alpha}\frac{\partial x^j}{\partial\beta} \\ &= \frac{1}{2}\left(\frac{\partial U_i}{\partial\beta}\frac{\partial x^i}{\partial\alpha}+\frac{\partial U_j}{\partial\alpha}\frac{\partial x^j}{\partial\beta}\right) \\ &= \frac{1}{2}\left[\partial_\beta(U_i\mathcal{E}^i_\alpha) - U_i\partial_\beta\mathcal{E}^i_\alpha + \partial_\alpha(U_j\mathcal{E}^j_\beta) - U_j\partial_\alpha\mathcal{E}^j_\beta\right] \\ &= \frac{1}{2}\left[\partial_\beta U_\alpha - \mathbf{U}\partial_\beta\mathcal{E}_\alpha + \partial_\alpha U_\beta - \mathbf{U}\partial_\alpha\mathcal{E}_\beta\right]\,, \end{aligned} \tag{C8}$$

where some additional notations should be obvious: U_i is a cartesian component of the displacement vector, $\mathbf{U}$ is the full vector. Introducing the connection coefficients or Christoffel symbols (of the second kind)

$$\Gamma^\gamma_{\alpha\beta} = \mathcal{E}^\gamma\partial_\beta\mathcal{E}_\alpha\,, \tag{C9}$$

we can rewrite (C8) as

$$\begin{aligned} U_{\alpha\beta} &= \frac{1}{2}\left(U_{\alpha,\beta}+U_{\beta,\alpha}\right) - \frac{1}{2}\Gamma^\gamma_{\alpha\beta}U_\gamma - \frac{1}{2}\Gamma^\gamma_{\beta\alpha}U_\gamma \\ &= \frac{1}{2}\left(U_{\alpha;\beta}+U_{\beta;\alpha}\right)\,, \end{aligned} \tag{C10}$$

where the semicolon in the last line denotes a covariant derivative. This last result is evident - tensorial equations retain their invariant form when written with covariant derivatives. Since in a flat space the derivative with respect to a cartesian coordinate is automatically a covariant derivative, we could have written down the last equation from knowledge of the form of the small-strain tensor in cartesian coordinates.

The fastest way to calculate the Christoffel symbols seems to be via their definition (C9). There is an alternative formula using derivatives of the metric coefficients and known to most

physicists from general relativity courses, but while this produces the same results, it does so via lengthy intermediate expressions only. Since we will consider only the leading-order expression for $V_{\rm el}$, we give the connection coefficients only to that order as well. At order ϵ^0, the metric (13) becomes the unit tensor, so superficial consideration might suggest that, being defined via derivatives of the metric, the Christoffel symbols should all vanish. However, one has to be careful to first take derivatives and then collect terms of order one, because derivatives with respect to r produce a factor $1/\epsilon$ when rewritten in terms of the stretched coordinate ρ. Taking this into account, we find the following Christoffel symbols to generically be nonzero at leading order:

$$\begin{aligned}
\Gamma^r_{ss} &= -\kappa_1 \,, \\
\Gamma^r_{qq} &= -\kappa_2 \,, \\
\Gamma^r_{sq} &= \Gamma^r_{qs} = -\tau \,, \\
\Gamma^s_{rs} &= \Gamma^s_{sr} = \kappa_1 \,, \\
\Gamma^s_{rq} &= \Gamma^s_{qr} = \tau \,, \\
\Gamma^q_{rs} &= \Gamma^q_{sr} = \tau \,, \\
\Gamma^q_{rq} &= \Gamma^q_{qr} = \kappa_2 \,.
\end{aligned} \tag{C11}$$

All the remainig ones are either $O(\epsilon)$ or exactly zero.

The components of the strain tensor are

$$\begin{aligned}
U_{rr} &= \frac{1}{\epsilon} U_{r,\rho} \,, \\
U_{ss} &= U_{s,s} + \kappa_1 U_r + O(\epsilon) \,, \\
U_{qq} &= U_{q,q} + \kappa_2 U_r + O(\epsilon) \,, \\
U_{rs} &= \frac{1}{2}\left(U_{r,s} + \frac{1}{\epsilon} U_{s,\rho} \right) - \kappa_1 U_s - \tau U_q + O(\epsilon) \,, \\
U_{rq} &= \frac{1}{2}\left(U_{r,q} + \frac{1}{\epsilon} U_{q,\rho} \right) - \kappa_2 U_q - \tau U_s + O(\epsilon) \,, \\
U_{sq} &= \frac{1}{2}\left(U_{s,q} + U_{q,s} \right) + \tau U_r + O(\epsilon) \,.
\end{aligned} \tag{C12}$$

Since the left hand sides of these equations are of order 1, the terms having a factor $1/\epsilon$ can be of order 1 at most, too. This implies $U^{(0)}_{r,\rho} = U^{(0)}_{s,\rho} = U^{(0)}_{q,\rho} = 0$, hence the zeroth-order displacement components must not depend on ρ:

$$\begin{aligned}
U^{(0)}_r &= U^{(0)}_r(s,q) \,, \\
U^{(0)}_s &= U^{(0)}_s(s,q) \,, \\
U^{(0)}_q &= U^{(0)}_q(s,q) \,.
\end{aligned} \tag{C13}$$

From this and (C12), we can immediately conclude that several of the strain tensor components are independent of ρ at zeroth order as well:

$$\begin{aligned}
U^{(0)}_{ss} &= U^{(0)}_{ss}(s,q) \,, \\
U^{(0)}_{qq} &= U^{(0)}_{qq}(s,q) \,, \\
U^{(0)}_{sq} &= U^{(0)}_{sq}(s,q) \,.
\end{aligned} \tag{C14}$$

The new feature in comparison with the two-dimensional case is that even a shear component of the strain tensor will be continuous across the interface, i.e., in a simulation the nonsolid phase will possibly undergo a biaxial strain. This is not really a problem, keeping in mind that this phase is treated in simulations as if it were a solid phase with vanishing shear modulus. Shear strains in this phase do not correspond to anything physical, and there is neither a shear stress nor energy associated with them.

If we take $\lim_{|\mathbf{r}|\to\infty} p = p_0$ as boundary condition for the pressure in the nonsolid bulk phase, then we know from Eq. (C2) that the pressure will take that value everywhere, and we can integrate the equation for $\tilde{\Sigma}_{rr}$ from (C4) with a known integration constant. Writing the result out in terms of the strains [using (3)], we obtain, introducing the abbreviation $h_0 = h(\Phi^{(0)})$:

$$\begin{aligned}
&h_0 \left[2G U^{(0)}_{rr} + \lambda \left(U^{(0)}_{rr} + U^{(0)}_{ss} + U^{(0)}_{qq} \right) \right] \\
&\quad + (1-h_0)\tilde{\lambda} \left(U^{(0)}_{rr} + U^{(0)}_{ss} + U^{(0)}_{qq} \right) - p_0 = -p_0 \,.
\end{aligned} \tag{C15}$$

We know the ρ dependence of all terms in this equation except $U^{(0)}_{rr}$, which suggests to solve for the latter quantity. This results in

$$U^{(0)}_{rr} = -\left(U^{(0)}_{ss} + U^{(0)}_{qq} \right) \left(1 - \frac{2Gh_0}{(2G+\lambda-\tilde{\lambda})h_0 + \tilde{\lambda}} \right) \,. \tag{C16}$$

The equations for $\tilde{\Sigma}^{(0)}_{sr}$ and $\tilde{\Sigma}^{(0)}_{qr}$ from (C4) imply together with the boundary conditions (C6) and (C7) that $U^{(0)}_{sr} = U^{(0)}_{qr} = 0$. Then Eq. (8) turns into

$$\begin{aligned}
V^{(0)}_{\rm el} = G &\left[\left(U^{(0)}_{rr} \right)^2 + \left(U^{(0)}_{ss} \right)^2 + \left(U^{(0)}_{qq} \right)^2 + 2 \left(U^{(0)}_{sq} \right)^2 \right] \\
&+ \frac{\lambda - \tilde{\lambda}}{2} \left(U^{(0)}_{rr} + U^{(0)}_{ss} + U^{(0)}_{qq} \right)^2 \,,
\end{aligned} \tag{C17}$$

and we can conclude from (C16) and (C14) that the elastic potential depends on ρ only via h_0. Abbreviating $tr_{2\rm D} U^{(0)} = U^{(0)}_{ss} + U^{(0)}_{qq}$ and $X = (2G + \lambda - \tilde{\lambda})h_0 + \tilde{\lambda}$, we get the compact form

$$\begin{aligned}
V^{(0)}_{\rm el} =& G \left(tr_{2\rm D} U^{(0)} \right)^2 \left[1 - \frac{2Gh_0}{X} - \frac{2Gh_0\tilde{\lambda}}{X^2} \right] \\
&+ G \left[\left(U^{(0)}_{ss} \right)^2 + \left(U^{(0)}_{qq} \right)^2 + 2 \left(U^{(0)}_{sq} \right)^2 \right] \,.
\end{aligned} \tag{C18}$$

According to (D9) and (D10), we have

$$\bar{V}^{(0)}_{\rm el} = \frac{\int_{-\infty}^{\infty} V^{(0)}_{\rm el} \left(\partial_\rho \Phi^{(0)} \right)^2 d\rho}{\int_{-\infty}^{\infty} \left(\partial_\rho \Phi^{(0)} \right)^2 d\rho} = \int_0^1 V^{(0)}_{\rm el} dh_0 \,, \tag{C19}$$

so the only integral that actually necessitates a calculation when integrating (C18) is

$$\begin{aligned}
&\int_0^1 \left(\frac{2Gh_0}{X} + \frac{2Gh_0\tilde{\lambda}}{X^2} \right) dh_0 \\
&\quad = \frac{2G}{(2G+\lambda-\tilde{\lambda})^2} \int_{\tilde{\lambda}}^{2G+\lambda} \frac{(X-\tilde{\lambda})(X+\tilde{\lambda})}{X^2} dX \\
&\quad = \frac{2G}{2G+\lambda} \,,
\end{aligned} \tag{C20}$$

all the other integrals reduce to integrating a constant from zero to one.

We obtain

$$\bar{V}_{\rm el}^{(0)} = \frac{G\lambda}{2G+\lambda}\left(tr_{\rm 2D}U^{(0)}\right)^2 + G\sum_{\bar{\alpha},\bar{\beta}}\left(U^{(0)}_{\bar{\alpha}\bar{\beta}}\right)^2 . \qquad \text{(C21)}$$

Note that both terms are interface scalar invariants, taking the same form in any (2D) coordinate system.

To relate this to the sharp-interface formula (1), we should transform it into an expression in terms of surface quantities, belonging to the outer equations. We have

$$\begin{aligned} u^{(0)}_{ss} &= U^{(0)}_{ss}(s,q)\,, \\ u^{(0)}_{qq} &= U^{(0)}_{qq}(s,q)\,, \\ u^{(0)}_{rr} &= -\frac{\lambda}{2G+\lambda}\left(U^{(0)}_{ss}+U^{(0)}_{qq}\right)\,, \end{aligned} \qquad \text{(C22)}$$

the last equation following from (C16) by taking the limit $\rho \to -\infty$.

In the following, we drop the superscript (0). Hooke's law together with (C22) provides us with

$$\begin{aligned} u_{ss}+u_{qq} &= \frac{1-\nu}{E}\left(\sigma_{ss}+\sigma_{qq}-2\sigma_{rr}\right)\,, \\ u_{ss}-u_{qq} &= \frac{1+\nu}{E}\left(\sigma_{ss}-\sigma_{qq}\right)\,, \end{aligned} \qquad \text{(C23)}$$

and the prefactors are related to the Lamé constants by $(1-\nu)/E = (2G+\lambda)/[2G(2G+3\lambda)]$ and $(1+\nu)/E = 1/2G$.

Inserting (C23) into (C21) and renaming σ_{rr} into σ_{nn}, it is straightforward to show that

$$\begin{aligned} \bar{V}_{\rm el}^{(0)} =& \frac{1+\nu}{2E}\sum_{\bar{\alpha},\bar{\beta}}\left(\sigma_{\bar{\alpha}\bar{\beta}}-\sigma_{nn}\delta_{\bar{\alpha}\bar{\beta}}\right)^2 \\ & -\frac{\nu}{2E}\Big[\sum_{\bar{\alpha}}\left(\sigma_{\bar{\alpha}\bar{\alpha}}-\sigma_{nn}\right)\Big]^2\,, \end{aligned} \qquad \text{(C24)}$$

which is, up to a factor, of $1/\rho_s$ the elastic part of the chemical potential of Eq. (1), just written in curvilinear coordinates instead of cartesian ones. It is clear from this result that if we set [in Eq. (66)] $M = \gamma M^* = \gamma D_s/\rho_s$, Eq. (50) will become identical to Eq. (6) from the sharp-interface model, which completes the proof that the phase-field model of Sec. V asymptotically approaches the sharp-interface model of Sec. II.

APPENDIX D: USEFUL PROPERTIES OF THE PHASE FIELD FUNCTIONS

In order to simplify it for the reader to find the actual relationships for the various functions involving the phase-field that are used in the text, they are collected here for reference (and concreteness). Often only certain properties but not the precise form of these functions is important.

The chosen double-well potential is

$$f(\phi) = \phi^2(1-\phi)^2\,. \qquad \text{(D1)}$$

Its derivative is given by

$$f'(\phi) = 2\phi(1-\phi)(1-2\phi)\,. \qquad \text{(D2)}$$

The "volume fraction function" $h(\phi)$ is

$$h(\phi) = \phi^2(3-2\phi)\,, \qquad \text{(D3)}$$

having the derivative

$$h'(\phi) = 6\phi(1-\phi)\,. \qquad \text{(D4)}$$

Then a useful observation is that

$$f(\phi) = \left(\frac{1}{6}h'(\phi)\right)^2\,. \qquad \text{(D5)}$$

To solve the ordinary differential equation satisfied by the zeroth-order inner solution

$$\partial_{\rho\rho}\Phi^{(0)} - 2f'(\Phi^{(0)}) = 0\,, \qquad \text{(D6)}$$

with boundary conditions $\lim_{\rho\to-\infty}\Phi^{(0)}(\rho) = 1$ and $\lim_{\rho\to\infty}\Phi^{(0)}(\rho) = 0$, we multiply by $\partial_\rho\Phi^{(0)}$, integrate and take the square root (with the correct sign) to obtain

$$\partial_\rho\Phi^{(0)} = -2\Phi^{(0)}(1-\Phi^{(0)}) = -\frac{1}{3}h'(\Phi^{(0)})\,, \qquad \text{(D7)}$$

which can be solved by separation of variables. The solution is, up to a translation in ρ, given by

$$\Phi^{(0)} = \frac{1}{2}(1-\tanh\rho)\,. \qquad \text{(D8)}$$

Requiring the position of the interface to be at $\rho = 0$ fixes the choice out of the one-parameter set of solutions, present due to the translational invariance of the differential equation.

With the help of the second equality of (D7), it is easy to calculate certain integrals appearing in the asymptotic analysis. Those integrals typically contain the factor $\left(\partial_\rho\Phi^{(0)}\right)^2$; to do the integral, it is then beneficial to replace one of the factors (and only one) with $-h'(\Phi^{(0)})/3$. Integrals obtained this way have the structure

$$\begin{aligned} I &= \int_{-\infty}^{\infty} d\rho\; f(h(\Phi^{(0)}))\;\left(\partial_\rho\Phi^{(0)}\right)^2 \\ &= -\frac{1}{3}\int_{-\infty}^{\infty} d\rho\; f(h(\Phi^{(0)}))\,h'(\Phi^{(0)})\,\partial_\rho\Phi^{(0)} \\ &= -\frac{1}{3}\int_1^0 d\Phi^{(0)}\; f(h(\Phi^{(0)}))h'(\Phi^{(0)}) = \frac{1}{3}\int_0^1 dh_0\; f(h_0)\,. \end{aligned} \qquad \text{(D9)}$$

This way, one arrives, for example, at

$$\int_{-\infty}^{\infty}\left(\partial_\rho\Phi^{(0)}\right)^2 d\rho = \frac{1}{3}\,. \qquad \text{(D10)}$$

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